Available online at www.sciencedirect.com

ScienceDirect

materialstoday: PROCEEDINGS

Materials Today: Proceedings 3S (2016) S258 – S265

Proceedings of the International Conference on Diamond and Carbon Materials

Photoluminescence of carbon dots embedded in a SiO_2 matrix

F. Messina*, L. Sciortino, G. Buscarino, S. Agnello, F. Gelardi, M. Cannas

Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Via Archirafi 36, 90123 Palermo (Italy).

Abstract

We synthetized carbon dots by a pyrolitic method, and studied their photoluminescence in aqueous environment and upon trapping in a solid matrix. To this aim, we devised a facile procedure allowing to embed the dots in amorphous SiO_2, without the need of any pre-functionalization of the nanoparticles, and capable of yielding a brightly photoluminescent monolith. Experimental data reveal a remarkable similarity between the emission properties of carbon dots in water and in SiO_2, suggesting that the chromophores responsible of the photoluminescence undergo only weak interactions with the environment. Time-resolved photoluminescence data reveal that the typical photoluminescence tunability of these dots mostly arises, in the present case, from the co-existence of two independent emission bands. These two signals have different emission peak positions (2.8-2.9 and 2.2-2.3 eV respectively) and decay lifetimes (7.0 and 9.0 ns respectively), while their intensity ratio is controlled by the excitation wavelength.

Selection and Peer-review under responsibility of the chairs of the International Conference on Diamond and Carbon Materials 2014.

Keywords: Carbon dots; photoluminescent nanocarbons; photoluminescent silica monolith; time-resolved photoluminescence.

1. Introduction

Carbon dots (CDs) are an emerging family of nanomaterials currently attracting a vast scientific interest since the first reports appeared between 2004 and 2007 [1-3]. CDs can be produced by several methods, such as electrochemical oxidation of graphite [4-5], laser ablation of carbonaceous materials [6-8], thermally- or microwave-induced decomposition of organic molecules in solution [9-12]. Broadly speaking, they can be described as quasi-

* Corresponding author. Tel.: +3909123891773
E-mail address: fabrizio.messina@unipa.it

Selection and Peer-review under responsibility of the chairs of the International Conference on Diamond and Carbon Materials 2014.
doi:10.1016/j.matpr.2016.02.043

spherical nanoparticles composed of partially oxidized carbon, with sizes in the 1-10 nm range. Indeed, the structure of CDs is rather synthesis-dependent, carbon atoms being arranged in variable combinations of sp^2 and sp^3 hybridizations, and with oxygen contents ranging from 20 to 50% [13-14]. The most interesting properties of CDs, however, are in the optical domain. In fact, these carbonaceous nanoparticles, provided that their surface is properly passivated, are systematically found to emit bright visible photoluminescence (PL) [13-15]. This property, essentially unparalleled by other carbon nanomaterials, is particularly appealing because CDs are also reportedly nontoxic [16-17], and can be easily dispersed in water in large concentrations due to the presence of many polar functional groups at the surface. Besides, the PL color can be typically adjusted across the visible by simply changing the excitation wavelength, which is usually referred to as the tunability of CD emission [2,18]. For instance their emission band, typically very broad ($\approx$0.5 eV or more at half maximum) and unstructured, was reported in ref. [18] to shift from 3.1 to 2.0 eV when the excitation was moved from 3.9 to 2.5 eV, or from 2.8 to 1.9 eV when the excitation was scanned from 3.1 to 2.0 eV [2]. Overall, CDs are often described as an emerging carbonaceous equivalent of photoluminescent semiconductor nanoparticles such as CdSe, resembling many of their optical and photo-chemical properties [15], but with the advantage of an inherent biocompatibility. CDs are the subject of an increasing interest inspired by their large potential for applications in bio-imaging [16-17,19-20], photocatalysis and solar energy harvesting [21-22], light-emitting devices [23-24], nano-sensors [8,25-27], and more.

Despite a few years of intense research, many basic questions still stand on the fundamental photo-physics of CDs. In particular, the very nature of the electronic transitions responsible of their PL is widely debated. Some experiments provided evidence that the chromophores responsible of the emission are sp^2-carbon domains constituting (or embedded into) the core of CDs, resembling optically-active polyaromatic molecules [21]. However, the emission may as well arise from surface-related states [2,15], as also suggested by the large pH-dependence and sensitivity to surface passivation reported by many studies. Also the origin of the emission tunability of CDs is poorly understood so far, beyond the shared understanding that such an effect stems from a large inhomogeneity affecting the spectroscopic properties of the emitting chromophores [13]. The existing studies on CDs have mostly addressed their properties in liquid phase, and especially water. In recent times, an increasing effort is being devoted to develop CD-based solid materials, in view of the potential solid-state applications of their light emission. Thus, a few works have lately reported the synthesis of photoluminescent solids embedding highly dispersed CDs [28-30], or photoluminescent solid monoliths and thin films fabricated by the formation of a dense network of CDs [31-32]. Indeed, the procedures capable of effectively trap CDs in solid-state while preserving their characteristic emission capability can be relatively elaborate and require pre-functionalization of the dots [28]. Furthermore, the general issue of whether and how changing the environment around CDs (e.g. by trapping them in a solid, or by changing solvent polarity) influences their optical properties, and the extent to which environmental fluctuations contribute to the overall inhomogeneity are scarcely explored problems so far, due to a lack of dedicated studies. Here we report a novel and facile route to prepare glass monoliths containing CDs. Our low-cost synthesis method produces solids with high optical quality preserving the attractive photoluminescence properties of CDs. At the same time, these materials offer a platform to investigate the environmental effects on the optical properties of such photoluminescent nanocarbons.

2. Materials and Methods

Citric acid monohydrate, urea, ethanol and TMOS (tetramethyl orthosilicate) were acquired from Sigma Aldrich and used without further purification in the synthesis described in the next section. PL spectra were recorded on an intensified CCD camera upon sample excitation by a tunable laser system consisting in an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser (5 ns pulses at 10 Hz repetition rate). PL measurements were excited by laser pulses having energy densities in the range E=50-100 $\mu J/cm^2$/pulse, as estimated by a power meter. Within this range of excitation intensities, we verified the PL intensity to depend linearly on the excitation power (at least for E<500 $\mu J/cm^2$), without changes of the emission shape; hence we normalized each spectrum for the excitation energy density used to acquire the measurement. The CCD camera was electronically triggered so as to record the emission spectra in a definite time window (0.5 ns time resolution) with respect to laser pulses. The emission spectra shown here were recorded in a time window of 100 ns duration, delayed of $\approx$3-5 ns from the laser. This choice allowed minimizing the contribution of scattered laser light while essentially capturing the entire

emission signal, which decays on a time scale of a few nanoseconds (see next section). The decay kinetics of the PL signals were obtained by recording spectra at variable delays from the laser pulse, and extracting the time dependence of the emission intensity at the peak of the band. We analyzed the size distribution of CDs by an atomic force microscope (AFM). Tapping mode amplitude modulation AFM measurements were performed by a Multimode V (Veeco Metrology) scanning probe microscope, equipped with a conventional piezoscanner (maximum xy range ≈14 μm and maximum z range ≈ 3.6 μm) and a four-segment photodetector for cantilever deflection monitoring. We used Pointprobe® Plus Silicon-SPM-probes with Al backside reflex coating, having a resonance frequency ≈300 kHz and a tip apical diameter of ≈10 nm. All the scans were executed at room temperature and in N_2 atmosphere, with a 2 nm/s tip velocity on the surface. The samples were prepared by depositing a drop of an aqueous suspension of CDs on a mica surface, having a surface roughness (rms) < 0.3 nm.

3. Results and Discussion

We prepared CDs via hydrothermal decomposition of organic molecules, well-established in the literature as a straightforward method to prepare highly photoluminescent carbonaceous nanoparticles [9-12]. A precursor aqueous solution of citric acid (300 g/L) and urea (300 g/L) was heated up to the boiling point until complete evaporation of water occurred. Thus we obtained a powder which was dried in vacuum at room temperature for 90 minutes. The obtained nanopowder can be easily re-dispersed in polar solvents, especially water (up to at least 15 gL^{-1}), forming suspensions which remain stable for months and cannot be separated by centrifugation up to 12000 rpm. The use of urea in the preparation allows to introduce nitrogen in the synthetized nanomaterial, which was repeatedly reported to enhance the PL of CDs [10,12,26,30]. As expected, AFM analysis confirms indeed that the synthetized material consists of sub-10 nm carbonaceous nanoparticles, consistent with previous reports for CDs prepared by a variety of synthetic methods [13-14]. A typical AFM image of a sample obtained by depositing a drop of the aqueous suspension on a mica substrate is shown in Fig. 1A. From this AFM image we obtain the statistical distribution of topographic heights shown in Figure 1B. The latter indicates that the average size of these CDs is about 3 nm.

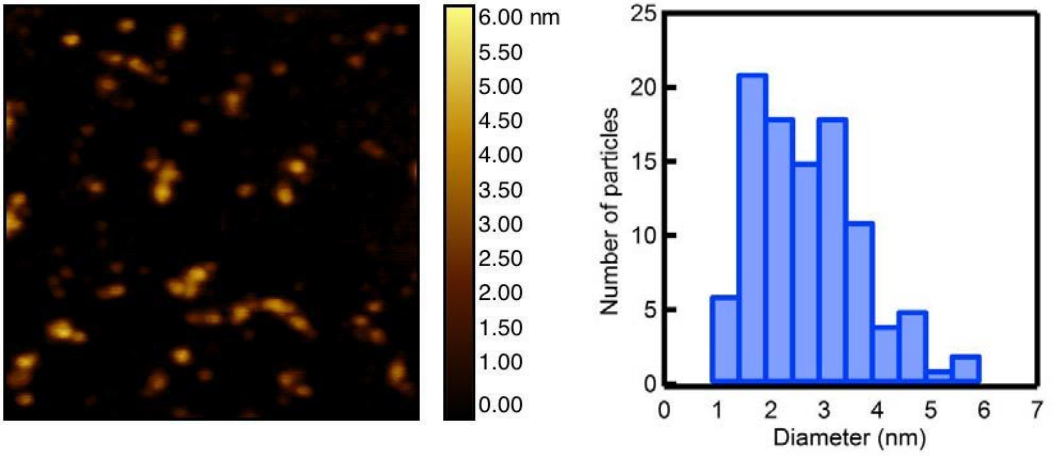

Fig. 1. Typical AFM image (1 μm x 1 μm) of CDs obtained by thermal decomposition of citric acid and urea. The sample is produced by depositing a drop of the aqueous suspension of CDs on a mica surface. Size distribution of CDs as estimated by the analysis of AFM images.

CDs obtained by this procedure were dispersed in H_2O at a concentration of 0.05 g/L, and their PL was measured under tunable laser excitation. The nanoparticles are found to be strongly emissive upon excitation at wavelengths spanning from the deep ultraviolet to the visible. At the same time, both the intensity and the peak position of the emission strongly change with the excitation wavelength, as shown in Figure 2A and 2B. Normalized emission

spectra (Figure 2B) show that the emission peak shifts from ≈2.8 eV to ≈2.2 eV when the excitation photon energy moves from 3.50 to 2.43 eV. As a consequence, the PL color of the CD solution can be widely tuned from the blue to the green by scanning the excitation wavelength, which is a characteristic behavior of CD photoluminescence [2][18].

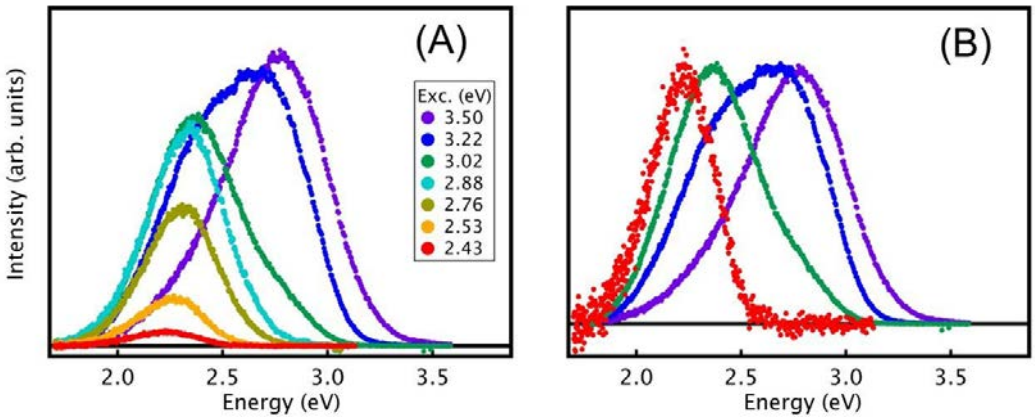

Fig. 2. Photoluminescence spectra of carbon dots in aqueous solution measured upon excitation at different photon energies (panel A). Normalized emission spectra (panel B) highlighting the tunability of CD photoluminescence across the visible when scanning the excitation.

On these grounds, we successfully synthetized a silica monolith embedding CDs by using a sol-gel preparation method. A 1.8 g mass of the aqueous solution of CDs was mixed with 6.16 g ethanol and 3.62 g TMOS to prepare the sol. Before gelification, an aliquot of the sol was moved to a sealed container used as a mold, and opened only after a few days. Then, the gels exhibited spontaneous shrinkage and became glasses (hereafter referred to as CD@SiO_2) with remarkable optical quality (inset of Figure 3B). The entire process was carried out at room temperature. The resulting solid samples are visually homogeneous, mechanically stable, with no signs of CD aggregation or surface irregularities. Notably, this remarkably simple procedure does not require any pre-functionalization of CDs.

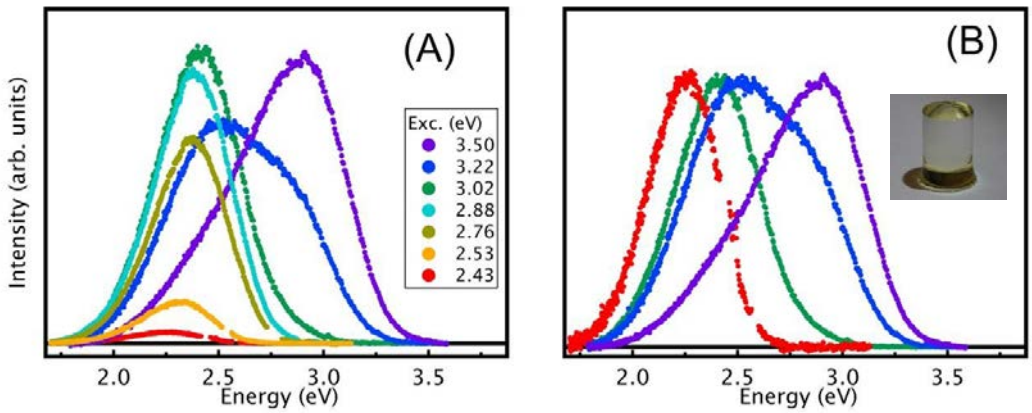

Fig. 3. Photoluminescence spectra of the CD@SiO_2 sample synthetized as described in the text, and measured under excitation at different photon energies (panel A) from the near UV to the visible. Normalized emission spectra (panel B). Inset of panel B: photograph of a CD@SiO2 sample, cylindrically-shaped with a diameter of 5 mm.

These solid hosts are found to preserve the characteristic bright photoluminescence of CDs, as obvious from Figure 3 where we show the emission collected from the CD@SiO_2 sample when excited by tunable laser light. Similarly to the liquid sample, the photoluminescence of CD@SiO_2 shifts from $\approx$2.9 to $\approx$2.3 eV when the excitation is scanned from 3.50 to 2.43 eV. Thus, from a practical point of view the CD@SiO_2 sample turns out to be a material potentially suitable for optical applications, in that it preserves the photoluminescence capabilities of CDs. Furthermore, the sample does not show any sign of optical damage upon laser excitation up to several mJ/cm^2/pulse at least.

A few works in the literature reported that the photoluminescence signal of CDs comprises two co-existing emission bands, a situation referred to as dual emission [11]. These two independent emission signals were interpreted as arising from core- and surface-related emission mechanisms, respectively [11,33]. Indeed, the shape of the PL we record here both in liquid phase and in SiO_2 suggests the presence of two contributions, hereafter named Signal I and II. To better emphasize this point we report in Figure 4 a few selected spectra detected from liquid-phase CDs (panels A-C) and CD@SiO_2 (panels D-F). In both samples a transition of the shape of the PL band is clearly observed when the excitation is scanned from $\approx$3.0 eV to $\approx$ 3.5 eV. All the signals in Fig. 4 can be reproduced by two Gaussian bands associated to signal I and signal II, peaking at 2.2-2.4 eV (green) and 2.8-2.9 eV (blue) respectively, and whose relative intensity ratio depends on excitation. In particular, excitation at 3.02 eV essentially excites a single emission band, that is signal I, with only a minor contribution of signal II, if any (see Fig. 4A and 4D). More in general, only signal I is excited by any photon energy smaller or equal of 3.1 eV, although the peak moves with excitation energy (see Fig. 2 and 3). In contrast, when the excitation is moved to 3.22 eV, signals I and II coexist with comparable intensities, as obvious from the shape of the band and its Gaussian decomposition (see Fig. 4B and 4E). Finally, excitation at 3.50 eV or larger energies preferentially excites signal II, although signal I never disappears completely (see Fig. 4C and 4F).

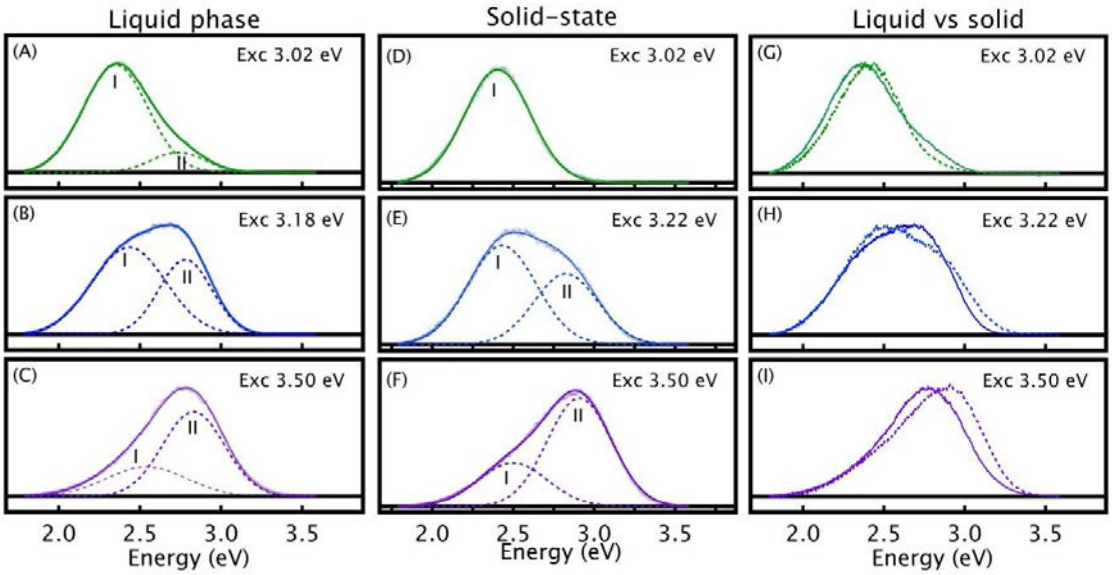

Fig. 4. PL spectra of CDs in solution (panels A,B,C) and CD@SiO_2 (panels D,E,F), as measured at three different photon energies, highlighting the transition between preferential excitation of signal I and signal II. The PL spectra are fitted by a linear combination of two Gaussian bands corresponding to signals I and II (see text). Fitting parameters are reported in Table I. Panels G,H,I compare the normalized PL spectra measured in the two samples at the three selected excitation energies.

The parameters obtained by Gaussian fitting of the PL spectra are reported in Table I. The intensity ratio between signal I and II is strongly excitation dependent in this range of excitation. We also observe small excitation-dependent changes of the peak position and full width at half maximum (FWHM) of either signal. Finally, we note that at any given excitation energy the overall shape of the PL is very similar, but not identical, in the two samples, as shown by the comparisons in panels G-I.

Table I. Spectral parameters and intensity ratios between Signal I and II as obtained by fitting the PL spectra of the two samples at three representative excitation energies with a linear combination of two Gaussian functions. N.D. stands for "not detected".

	Signal I		**Signal II**		**Intensity ratio**
Liquid phase CDs	**Peak (eV)**	**FWHM (eV)**	**Peak (eV)**	**FWHM (eV)**	**I/II**
Exc 3.02 eV	2.35±0.01	0.47±0.02	2.74±0.01	0.40±0.02	5.5
Exc 3.18 eV	2.43±0.01	0.53±0.02	2.78±0.01	0.38±0.02	1.1
Exc 3.50 eV	2.54±0.01	0.58±0.02	2.83±0.01	0.44±0.02	0.5
CD@SiO_2	**Peak (eV)**	**FWHM (eV)**	**Peak (eV)**	**FWHM (eV)**	**I/II**
Exc 3.02 eV	2.40±0.01	0.48±0.02	N.D.	N.D.	∞
Exc 3.18 eV	2.43±0.01	0.50±0.02	2.83±0.01	0.47±0.02	1.4
Exc 3.50 eV	2.50±0.01	0.50±0.02	2.90±0.01	0.47±0.02	0.4

Bands I and II can be also distinguished from their decay kinetics, shown in Figure 5. The two lifetime measurements reported in the plot were obtained by taking the intensity at the peak of the emission band recorded at two different excitation energies, 3.49 and 2.53 eV, chosen as to prevalently excite signal II and I respectively. Both emissions decay within a few nanoseconds, suggesting a strongly dipole-allowed electronic transition to be responsible of the photoluminescence. However, while signal I (decay kinetics at 2.53 eV) disappears with a fairly exponential kinetics with a lifetime of 7.0±0.5 ns (as obtained by least-square fitting), the decay of signal II (decay kinetics at 3.49 eV), significantly deviates from a pure exponential and has a slower decay (lifetime of 9.0±0.5 ns, defined as the time at which the intensity drops of a factor 1/e). Likely, the non-exponential behavior of signal II could be an apparent effect due to the residual contribution of signal I even at the excitation energy (3.5 eV) where signal II prevails. In fact, Fig. 4C and 4F show that signal I does not completely disappear even when samples are excited at 3.5 eV.

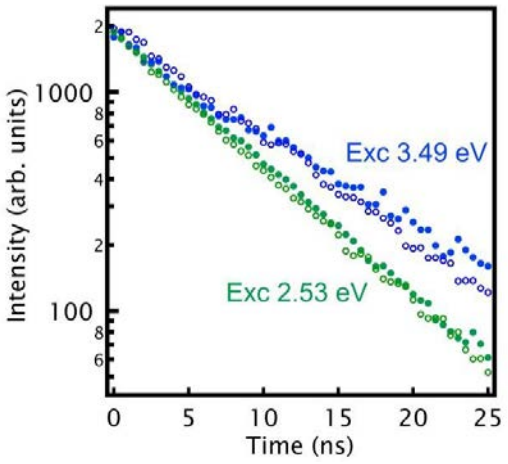

Fig. 5. PL decay kinetics recorded for CDs in aqueous solution (full symbols) or embedded in SiO_2 (empty symbols), as measured under excitation at 3.49 eV (corresponding to signal II – see text) or 2.53 eV (signal I – see text). The measurements were obtained by taking the peak emission intensity as a function of time delay.

The photoluminescence tunability of CDs is usually ascribed to the fact that different wavelengths select different subsets out of a heterogeneous population of chromophores with continuously varying electronic gaps [13]. Present data reveal that tunability actually arises from a combination of two conceptually different effects. The predominant one is actually the changing ratio between signals I and II when the excitation wavelength is scanned (see Fig. 4 and Table I). This effect only allows to tune the emission color from the green to the blue when the excitation is scanned from 3.0 to 3.5 eV. Beyond that, the peak position of either signal is excitation-sensitive in itself, and continuously changes with excitation wavelength. This second effect, already visible in Table I, can be clearly observed in Figure 2B and 3B by comparing the normalized spectra excited at 3.02 and 2.43 eV: both are due to signal I, which undergoes a redshift of about 0.15 eV.

We finally discuss the close similarity we observe between CD photoluminescence in liquid and solid phase. Broadly speaking, this finding implies that the interactions between CDs and the amorphous SiO_2 matrix are weak enough not to hinder or strongly alter the electronic transition responsible of the emission. In this respect is it particularly notable that the decay kinetics of both PL bands are virtually identical (Figure 5) in liquid and solid phase. Interestingly, the same degree of tunability is observed in the two samples, with only small changes in the width of the PL bands: for instance, the FWHM of the emission band of signal I, excited at 3.02 eV, is measured to be 0.47-0.48 eV for both aqueous CDs and CD@SiO_2, while the FWHM of signal II excited at 3.5 eV is 0.44 eV and 0.47 in liquid- and solid-phase CDs respectively. (see Table I) Incidentally, this suggests that inhomogeneity effects, dominating the spectral width of the emission bands, are essentially due to the nonequivalence of different dots, rather than to environmental-dependent fluctuations. On the other hand, Figures 4G-4I, as well as Table I, reveal minor, but appreciable, differences between aqueous and solid-state PL. Such changes affect the ratio between signals I and II, accompanied by small shifts (0.05 eV and 0.07 eV at the most, for signal I and II respectively) between liquid- and solid-phase PL bands. These shifts are apparently smaller than those observed when suspending CDs in solvents having different polarities and chemical properties [34]; these latter effects are generally proposed to be solvatochromic in nature, due to the different solvation of surface-exposed chromophores, claimed by many works to be mostly responsible of CD emission [2][15].

A possible interpretation of the present findings is that both chromophores (I and II) responsible of the PL of these CDs are well buried in the core of the nanoparticles, which explains why they are so weakly sensitive to environmental changes. This would contrast with previous interpretations of the dual emission of CDs as arising from independent core- and surface- emission mechanisms [11][33], because the two resulting PL bands should react very differently to a change of the surroundings. However, another possibility is that the local environment around CDs within the SiO_2 monolith is actually a very polar one, and thus relatively similar to the environment they experience in aqueous solution. In this scenario, the optical properties would be hardly affected when embedding the dots in the solid, even if the emission stems from surface states. Further studies are in progress to elucidate in more detail the interactions between CDs and SiO_2 that make possible the formation of stable CD@SiO_2 monoliths while essentially preserving the photoluminescence properties of the dots.

Conclusions

We studied by time-resolved photoluminescence spectroscopy the properties of CDs suspended in water and trapped in SiO_2. Their PL is found to arise from two co-existing and independent contributions, which can be distinguished by their emission spectral shape as well as by lifetime measurements. Indeed, the dual nature of the PL explains most of the emission tunability of these CDs. We reported a simple procedure allowing to embed carbon dots into a stable silica monolith with high optical quality, potentially suitable for solid-state optical applications. The main features of the photoluminescence of CDs, such as tunability and nanosecond decay kinetics, are weakly affected by trapping in SiO_2, which suggests the emission transitions to arise from chromophores well embedded in the core of the nanoparticles and thus weakly sensitive to environmental changes.

References

[1] X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker, W. A. Scrivens, J. Amer. Chem. Soc. 126 (2004) 12736.

[2] Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. Shiral Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. Monica Veca, S.-Y. Yie, J. Amer. Chem. Soc. 128 (2006) 7756.
[3] H. Liu, T. Ye, C. Mao, Angew. Chem. Int. Ed. 46 (2007) 6473.
[4] Q. L. Zhao, Z. L. Zhang, B. H. Huang, J. Peng, M. Zhang, D. W. Pang, Chem. Commun. 5116 (2008).
[5] L. Y. Zheng, Y.W. Chi, Y. Q. Dong, J. P. Lin, B. B. Wang, J. Am. Chem. Soc. 131 (2009) 4564.
[6] S.-L. Hu, K.-Y. Niu, J. Sun, J. Yang, N.-Q. Zhao, X.-W. Du, J. Mater. Chem. 19 (2009) 484.
[7] X. Li, H. Wang, Y. Shimizu, A. Pyatenko, K. Kawaguchi, N. Koshizaki, Chem. Commun. 47 (2011) 932.
[8] H. Goncalvez, P. A. S. Jorge, J. R. A. Fernandez, J. C. G. Estevez da Silva, Sensors Actuat. B 145 (2010) 702.
[9] X.Wang, K. Qu, B. Xu, J. Ren, X. Qu, J. Mater. Chem. 21 (2011) 2445.
[10] S. Qu, X. Wang, Q. Lu, X. Liu, L. Wang, Angew. Chem. Int. Ed. 51 (2012) 12215.
[11] M. J. Krysmann, A. Kelarakis, P. Dallas, E. P. Giannelis, J. Amer. Chem. Soc. 134 (2012) 747.
[12] Y. Yang, J. Cui, M. Zheng, C. Hu, S. Tan, Y. Xiao, Q. Yang, Y. Liu, Chem. Commun. 48 (2012) 380.
[13] S.N. Baker, G. A. Baker, Angew. Chem. Int. Ed. 49 (2010) 6726.
[14] H. Li, Z. Kang, Y. Liu, S.-T. Lee, J. Mater. Chem. 22 (2012) 24230.
[15] L. Cao, M. J. Meziani, S. Sahu, Y.-P. Sun, Acc. Chem. Res. 46 (2013) 171.
[16] S.-T. Yang, L. Cao, P. G. Luo, F. Lu, X. Wang, H. Wang, M. J. Meziani, Y. Liu, G. Qi, Y.-P- Sun, J. Amer. Chem. Soc. 131 (2009) 11318.
[17] Q.-Q. Shi, Y.-H- Li, Y- Xu, Y. Wang, X.-B. Yin, X.-W. He, Y.-K. Zhang, R. Soc. Chem. Adv. 4 (2014) 1563.
[18] D. Pan, J. Zhang, Z. Li, C. Wu, X. Yan, M. Wu, Chem. Commun. 46 (2010) 3681.
[19] L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. Monica Veca, D. Murray, S.-Y. Xie, Y.-P. Sun, J. Amer. Chem. Soc. 129 (2007) 11318.
[20] C. Liu, P. Zhang, F. Tian, W. Li, F. Li, W. Liu, J. Mater. Chem. 21 (2011) 13163.
[21] H. Li, X. He, Z. Kang, H. Huang, Y. Liu, J. Liu, S. Lian, C. H. A. Tsang, S.-T. Lee, Angew. Chem. Int. Ed., 49 (2010) 4430.
[22] P. Mirtchev, E. J. Henderson, N. Soheilna, C. M. Yip, G. A. Ozin, J. Mater. Chem. 22 (2012) 1265.
[23] F. Wang, Y.-H. Chen, C.-Y. Liu, D.-G. Ma, Chem. Commun. 47 (2011) 3502.
[24] X. Zhang, Y. Zhang, Y. Wang, S. Kalytchuk, S. V. Kershaw, Y. Wang, P. Wang, T. Zhang, Y. Zhao, H. Zhang, T. Cui, Y. Wang, J. Zhao, W. W. Yu, A. L. Rogach, ACS Nano 7 (2013) 11234.
[25] A. Zhu, Q. Qu, X. Shao, B. Kong, Y. Tian, Angew. Chem. Int. Ed. 51 (2012) 7185.
[26] Y. Dong, R. Wang, H. Li, J. Shao, Y. Chi, X. Lin, G. Chen, Carbon 50 (2012) 2810.
[27] A Cayuela, M. L. Soriano, M. Valcárcel, Analytica Chimica Acta 804 (2013) 246.
[28] Z. Xie, F. Wang, C.-Y. Liu, Adv. Materials 24 (2012) 1716.
[29] L. Zhou, B. He, J. Huang, Chem. Commun. 49 (2013) 8078.
[30] W. Kwon, S. Do, J. Lee, S. Hwang, J. K. Kim, S.-W. Rhee, Chem. Mater. 25 (2013) 1893.
[31] F. Wang, Z. Xie, H. Zhang, C.-Y. Liu, Y.-G. Zhang, Adv.Funct. Mater. 21 (2011) 1027.
[32] D. Pan, J. Zhang, Z. Li, Z. Zhang, L. Guo, M. Wu, J. Mater. Chem. 21 (2011) 3565.
[33] P. Yu, X. Wen, Y.-R. Toh, J. Tang, J. Phys. Chem. C 116 (2012) 25552.
[34] O. Kozák, K. K. R. Datta, M. Greplová, V. Ranc, J. Kašlík, R. Zbořil, J. Phys. Chem. C 117 (2013) 24991.